Second-generation biofuels by co-processing catalytic pyrolysis oil in FCC units

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ABSTRACT

Previous research showed that hydrodeoxygenated (HDO) pyrolysis-oils could successfully be co-processed with vacuum gasoil (VGO) in a labscale fluid catalytic cracking (FCC) unit to bio-fuels. Typically the hydrodeoxygenation step takes place at ∼300 °C under 200–300 bar of hydrogen. Eliminating or replacing this step by a less energy demanding upgrading step would largely benefit the FCC co-processing of pyrolysis oils to bio-fuels. In this paper a bio-oil that has been produced by catalytic pyrolysis (catalytic pyrolysis oil or CPO) is used directly, without further upgrading, in catalytic cracking co-processing mode with VGO. The results are compared to the co-processing of upgraded (via HDO) thermal pyrolysis oil. Though small but significant differences in the product distribution and quality have been observed between the co-processing of either HDO or CPO, they could be corrected by further catalyst development (pyrolysis and/or FCC), which would eliminate the need for an up-stream hydrodeoxygenation step. Moreover, the organic yield of the catalytic pyrolysis route is estimated at approximately 30 wt.% compared to an overall yield for the thermal pyrolysis followed by a hydrodeoxygenation step of 24 wt.%.

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1. Introduction

Due to the depletion of carbon fossil resources (oil, gas and coal) and increased efforts to mitigate CO₂ emissions, the production of liquid transportation fuels from biomass has become a booming research area [1]. Within the frame of the "20-20-20" objectives aiming to achieve 20% emissions reduction, 20% increase of renewable energy and 20% increase in energy efficiency by 2020 proposed by the EU, in close link with the the International Energy Agency "Energy Technology Perspectives 2020", a general consensus is to focus on bio-fuels that are not in net competition with food production, and to reach the objectives for fuel transportation either via blending or co-processing strategies. In that sense, non-competing lignocellulosic biomass sources derived from forestry and industrial wastes seem to be the most realistic feedstock for the production of a second generation of transportation fuels [2]. Lignocellulosic biomass can be converted to liquids by fast pyrolysis [2,3]. This technology is currently in its pilot pre-industrial stage [3]. Pyrolysis-oils are composed of a very complex mixture of oxygenated hydrocarbons (> 300) [4], the main constituents being acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols and phenol derivatives, as well as carbohydrates and derivatives,

and a large proportion (20–30 wt.%) of lignin-derived oligomers [5]. Due to their oxygen rich composition, they present a low heating value, immiscibility with hydrocarbon fuels, chemical instability, high viscosity and corrosiveness [6–10], restricting their direct use as fuels. The (partial) elimination of oxygen is thus necessary to transform the bio-oil into a liquid fuel that can compete with mineral oil refinery fuels. Two main types of upgrading processes are used to reject oxygen from pyrolytic bio-oils: hydrotreating or hydrodeoxygenation (HDO) and catalytic cracking. The former uses hydrogen to remove oxygen in the form of water from the initial thermal pyrolysis oil over mixed oxides and supported metal catalysts. The latter accomplishes the removal of oxygen in the form of water and carbon oxides, generally over acid catalysts (zeolites). An obvious drawback of the HDO process is the use of large amounts of hydrogen at elevated pressures while catalytic cracking does not require hydrogen. The latter leads to more olefinic and aromatic products.

An alternative to post-pyrolysis upgrading processes is a combined pyrolysis/deoxygenation step. The thermal pyrolysis step can be combined with the catalytic cracking step in one operation by replacing the silica sand in the fluidized bed reactor by an appropriate catalyst or by placing the catalyst directly in the freeboard space of the reactor. This is referred to as catalytic pyrolysis [11–31].

Research studies on catalytic pyrolysis have appeared in the open literature regularly since the 1980s, but their number has increased significantly during the last 5–6 years [11–31]. The KiOR

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Table 1
Properties of VGO, HDO and CPO.

Property	VGO	HDO	CPO
Density (g/cm^3, 25 °C)	0.8953	0.9323	nd
Sulfur (wt.%)	2.02	<0.01	<0.20
Nitrogen (wt.%)	0.07	<0.1	<0.10
Hydrogen (wt.%)	12.4	10	7
Carbon (wt.%)	85.4	69	66
Oxygen (wt.%)	Traces	21	27
H_2O (wt.%)	Traces	3	11

Table 2
^{31}P NMR analysis of the two bio-oils.

	HDO	CPO
Hydroxyl groups (mmol/g$_{oil}$)	1.4	0.6
Phenolic groups (mmol/g$_{oil}$)	1.4	3.1
Acidic groups (mmol/g$_{oil}$)	0.6	0.5

company has deposited a patent application on this process and is operating a pilot plant in the USA [32].

The studies are difficult to compare as there is a large variation of a number of parameters: biomass source (model compounds, wood, corn etc.), scale of operation (micrograms to kilograms), contact time, mode of contact between biomass and catalyst, biomass to catalyst ratio and the type of catalyst. Keeping this in mind some general trends can be discerned:

The addition of a catalyst to the thermal pyrolysis process results in a lower yield of bio-oil organic compounds. The lower oil yields stem from oxygen removal to water, CO_2 and CO, to coke formation on the catalyst and to an increase in hydrocarbon gas yield.

The yield of the oil fraction depends on the catalyst formulation. In a large number of studies ZSM-5 is reported to give the highest yield among other zeolites including commercial FCC (Fluid Catalytic Cracking) catalysts. Some bulk oxides, such as ZnO, CuO, Fe_2O_3 are reported to be good catalysts as well [11]. In addition, mesoporous MCM materials have been studied extensively [18,30,31]. The catalyst formulation not only has an effect on the bio-oil yield, but it also influences its composition leading thus to a better quality bio-oil.

This study reports on the co-processing of catalytic pyrolysis oil (CPO) with vacuum gasoil (VGO) in a Fluid Catalytic Cracking (FCC) labscale unit. The results are compared to co-processing of HDO-upgraded thermal pyrolysis oil with VGO in FCC [33–35], in order to assess the advantages and drawbacks of each upgrading strategy. FCC is one of the most important processes of a modern refinery because of its flexibility to changing feedstock and product demands. Its principal aim is to convert high molecular weight hydrocarbons to more valuable products, mainly gasoline [36–39].

2. Experimental

2.1. Materials

The elemental composition of the VGO is given in Table 1. Boiling point analysis (simulated distillation) showed that it contained a non-negligible fraction (4 wt.%) below 200 °C.

Thermal pyrolysis oil was obtained by flash pyrolysis of pine wood residue [40]. It contained 7.6 wt.% H, 40.6 wt.% C and 51.7 wt.% O. Its properties are reported in detail in reference [40]. 2 wt % iso-propanol was added to the thermal pyrolysis oil after which a top and bottom phase appeared. The filtered bottom phase of the pyrolysis oil (90%, containing 8.0 wt.% H and 40.7 wt.% C) was hydrogenated at 290 bar and 330 °C over a carbon supported ruthenium catalyst [41]. The density and elemental composition of the final HDO-oil are shown in Table 1, whereas the detailed elemental composition of the starting material is reported in reference [41].

Catalytic biomass pyrolysis was realized using a commercial lignocellulosic biomass (Lignocel HBS 150–500) originating from beech wood was used. Detailed analysis on this biomass can be found in reference [29]. Catalytic pyrolysis oil (CPO) was obtained in a pilot plant unit. This unit is described in more detail in reference [14]. A ZSM-5 catalyst with a surface area 38 m^2/g was employed for the catalytic pyrolysis at 482 °C. The oil composed

of two fractions, an aqueous and an oil fraction. Only the organic fraction was used during the test. The density and elemental composition of the final CPO is reported in Table 1.

Phosphor NMR analysis allows to quantify the oxygenated compounds into three groups of alcohols, phenols and acids [42]. Table 2 shows these quantities for both bio-oils. Size exclusion chromatography (SEC) was used to compare the molecular weight distribution of the two bio-oils. Although the molecular weights should not be taken as absolute values (polystyrene calibration), comparison showed that HDO oil contains components up to 1700 g/mol whereas CPO components go up to 2600 g/mol.

An equilibrated industrial FCC catalyst containing ∼15 wt.% Y-zeolite was used for VGO cracking and co-processing experiments. The equilibrated industrial FCC catalyst used in this study contains 15 wt.% Y-zeolite, 2.5 wt.% rare earth oxides, 240 ppm of Ni and 870 ppm of V.

2.2. Set-up

VGO cracking and co-processing (VGO + CPO or HDO cracking) experiments were performed in a fixed-bed quartz reactor (ID = 12 mm, L = 340 mm) containing 2.0 g of FCC catalyst at 1.2 bar and operated to mimic a series of FCC cycles. The equipment has been validated with respect to a microactivity test reactor for VGO cracking [43]. A thermocouple was located inside the catalyst bed. Argon was used as a carrier gas (flow = 100 ml/min). One reaction cycle consists of 1 minute cracking at 500 °C, 11 min of stripping under argon flow at 500 °C, 40 min regeneration under 20 vol.% of O_2 in Ar at 650 °C and 11 min purge. In order to obtain sufficient liquid for further analysis 6 reaction/regeneration cycles were performed for each run. During the cracking and stripping steps, the liquid product was collected in a glass receiver located at the exit of the reactor and kept at −50 °C. Meanwhile, the gases were collected in a gasbag. The amount of coke formed on the catalyst was estimated from the carbon dioxide production during the regeneration period, as measured by mass spectrometry.

Cracking was performed at three different catalyst to oil ratios (Cat/Oil) by changing the amount of feed injected into the reactor, but by keeping the amount of catalyst constant. The bio-oils were mixed directly with the VGO and injected with a HPLC pump. For the co-processing experiments reported here 10 wt.% of HDO or CPO was co-fed with VGO. The Cat/Oil ratio includes the weight of both HDO or CPO and VGO in calculating the feed weight. All cracking experiments have been run twice. A good reproducibility was obtained of the yield of the various fractions with typical deviations of a few percent (absolute).

2.3. Analysis

Gaseous products during cracking/stripping cycles were analyzed using an Agilent 3000A micro gas chromatograph using He as an internal standard. Gaseous products obtained during regeneration cycles were analyzed on-line by a mass spectrometer (VG-Prolab). This mass spectrometer (MS) was regularly calibrated for CO and CO_2 and He was used as an internal standard. The errors in the coke yields are estimated as less than ±5%.

Samples from the liquid products were analyzed on a HP6890 gas chromatograph equipped with an ASTM-2887 system and
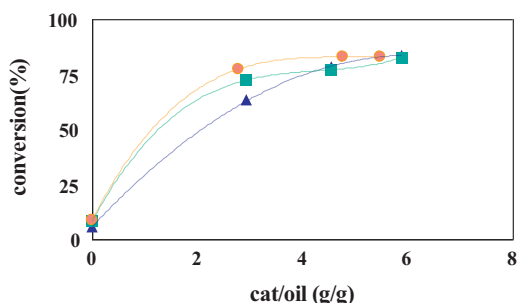
Fig. 1. Conversion versus Cat/Oil ratio for VGO processing (▲), HDO/VGO co-processing (■) and CPO/VGO co-processing (●).

analyzed according to their boiling point range. Liquid samples were also analyzed by a GC × GC system with a mass spectrometer as detector. In this work, only the total response of the MS detector is used as an indication of the evolution of specific compounds; thus providing a semi-quantitative analysis. Details of the analysis procedure have been reported in reference [33,42].

For every experiment it is possible to assess the yield of individual hydrocarbons or groups, and the following main groups were defined: dry gas (H_2, CO, CO_2, C1–C2 hydrocarbons), liquefied petroleum gas (LPG: C3–C4 hydrocarbons) gasoline (C5-221 °C boiling point), light cycle oil (LCO – 221–370 °C boiling point), bottom fraction (boiling point > 370 °C) and coke. The conversion is defined as a sum of the yields of dry gas, LPG, gasoline and coke. Mass balances in all the experiments are closed to 95%. The yield of each fraction is given by

$$\text{Yield of fraction } i = \frac{\text{mass of fraction } i}{\text{total mass in the feed}} \times 100 \qquad (1)$$

The water (produced during bio-oil upgrading) content in the liquid effluent was measured by the Karl-Fischer method. Oxygen *content* in the liquid effluent was determined by elemental analysis.

3. Results

The three cracking sequences run over the equilibrated FCC catalyst were performed by using different Cat/Oil ratios to vary the levels of conversion in a similar range for the 3 sequences considered:

 (i) pure VGO cracking at Cat/Oil ratios of 3.1, 6.0 and 8.9;
 (ii) 10 wt.% HDO/VGO co-processing at Cat/Oil ratios of 3–4–6;
(iii) 10 wt.% CPO/VGO co-processing at Cat/Oil ratios of 2.9–3.2–5.5 and 8.3.

The study was performed at different Cat/Oil ratios to observe the co-processing effect at different conversion levels.

As seen in Fig. 1, the conversion increases with the Cat/Oil ratio in all cases. However, this increase is more linear for pure VGO cracking, than for co-processing of either HDO or CPO where the conversion tends to reach rapidly its maximum value. Note that the non-zero conversion values at Cat/Oil = 0 for the co-processing experiments are due to the fact that a slight fraction of the added bio-oils as feedstock is considered as a product (gasoline range) as defined by the conversion given in Section 2.3.

Fig. 2 shows a comparison of the product yields for the VGO and the VGO/HDO or VGO/CPO mixture at similar values of the Cat/Oil ratio, i.e., at slightly different conversions as already seen in Fig. 1. As can be seen, co-feeding HDO or CPO at various Cat/Oil ratios induces some changes in the product distribution:

Co-processing of the bio-oils produces higher yields for dry gas, similar or slightly lower for LPG while the yields of gasoline are

slightly higher for CPO/VGO, the LCO yields are lower and the bottom are comparable to those corresponding to the cracking of VGO. A major effect is also observed on coke formation, which is almost two fold higher for co-processing as compared to VGO cracking.

As expected, co-processing also leads to the production of CO_2 and H_2O (not shown) from oxygenates decomposition: 0.25 and 0.5 wt.% CO_2 and approximately 1 and 1.5 wt.% H_2O for HDO and CPO co-processing, respectively. On the other hand the hydrogen production decreases during co-processing of VGO/HDO and drops even further during the co-processing of VGO/CPO (Fig. 2).

3.1. Gasoline range product quality

The GCxGC technique was used to explore in more detail the composition of the gasoline fraction as simulated distillation technique gave close yields for the gasoline fraction for VGO cracking and HDO co-processing while a slightly higher yield is observed for CPO coprocessing, especially at moderate conversion. At ∼80% conversion (Cat/Oil around 6), when the yields tend to be similar for all three types of feeds, it is interesting to see whether the compositions of the produced gasoline are similar as well. All the compounds are grouped in the following families: aliphatics, mono-, di, tri and tetra aromatics, and are shown in Fig. 3. The formation of all the aromatic products tends to decrease with increasing of the conversion in the case of VGO cracking and HDO/VGO co-processing. In contrast, it seems to pass through a minimum for the CPO/VGO co-processing at medium conversion, which clearly differentiates the gasoline quality for this case with significantly more aromatics at high conversion.

3.2. Oxygenates

The bio-oils contain typical oxygenated compounds such as acids, aldehydes, furans, guaiacols, syringols, alkylphenols, alkylbenzenes and hydrocarbons [4]. P-NMR analysis showed that all oxygenated compounds except the phenolic fraction have been converted. However, this roughly corresponds to the amount of CO_2 and H_2O formed, as well as the global oxygen content of the liquid fraction after reaction based on elemental analysis. As observed previously for the co-processing of HDO/VGO, co-processing of CPO/VGO also leads, even in larger amounts, to the presence of alkylphenols in the gasoline fraction. The presence of phenol and alkylphenols with side-chains up to C6 were observed. Fig. 3 shows the trends of the formation and consumption of different alkylphenols for both co-processing mixtures. Co-processing of both bio-oils lead to the formation and subsequent conversion of alkylphenols, but for the CPO the alkylphenol concentration is approximately two times higher than for the HDO.

4. Discussion

The results of co-processing either HDO or CPO indicate only moderate differences on the overall performance, though specific and significant effects are noted on the product quality. The main differences between VGO processing and HDO/VGO co-processing (increased coke production, less hydrogen, more olefins and aromatics and the presence of alkyl-phenols) and a tentative explanation of the effects of oxygenates on the reaction mechanism have been discussed in detail by our group [33–35,43] as well as by others [5,41,44]. Here we will restrict the discussion on the differences observed on the cracking products quality, focusing to the origin of the bio-oil obtained either from thermal flash pyrolysis followed by a hydrodeoxygenation step or directly from catalytic pyrolysis.

The composition of both bio-oils is given in Tables 1 and 2. CPO contains more oxygen and less hydrogen than HDO oil. This is due
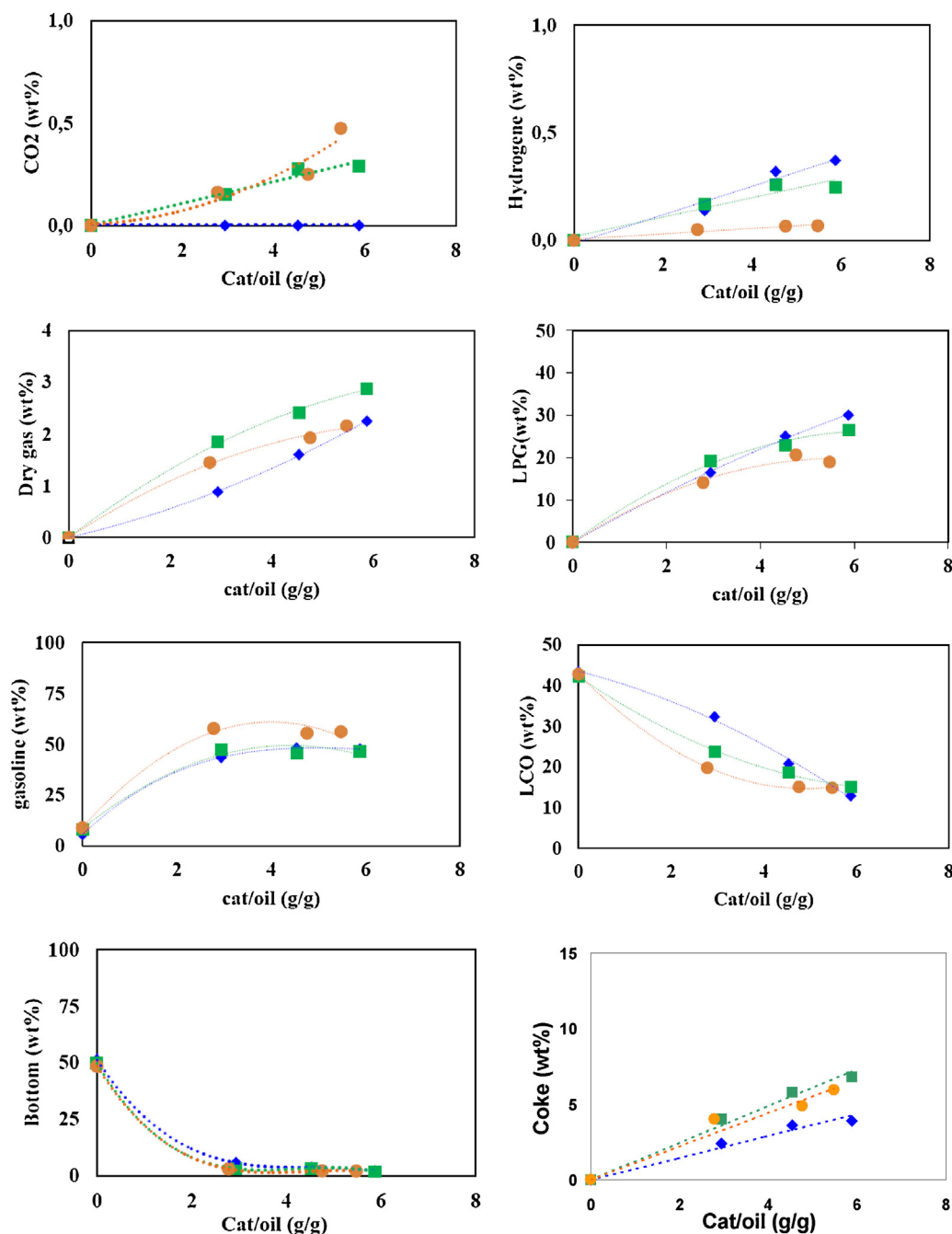
Fig. 2. Product distribution as a function of the Cat/Oil ratio for VGO processing (♦), HDO/VGO co-processing (■) and CPO/VGO co-processing (●).

to the fact that the HDO has already undergone a hydrogenation step, which is more efficient in eliminating oxygen than the catalytic cracking during the catalytic pyrolysis step. In turn, during the CPO process, any hydrogen (hydride or proton) arising from the catalytic cracking process (e.g., via H transfer) will be used for any deoxygenation step, leading to more water formed and to a lower hydrogen content.

This excess of oxygen in CPO as compared to HDO will have the same effect during co-processing where more hydrogen will be consumed via water formation, explaining the lower hydrogen production (Fig. 2) compared to HDO/VGO and the higher concentration of olefins and aromatics, especially at high feed conversion (Fig. 3).

Another specificity of the CPO is that it contains heavier components (as observed by size exclusion chromatography) most likely consisting of lignin polymers. This likely stems from the fact that the heavy lignin polymer fragments can hardly be cracked during catalytic pyrolysis within the too narrow pores of the ZSM-5 catalysts. The larger oxygenated molecules will adsorb preferentially on the outside of the zeolite framework or on the silica-alumina matrix, as they cannot enter the micropores. The cracking of the phenolic fragments requires the transfer of Brønsted sites protons, which are regenerated by the cracking of alkanes. This process leads to smaller molecules like alkylphenols and methoxyphenols as well as coke. In a second step, the formed alkylphenols and methoxyphenols can either be further dehydroxylated on the same sites of the outer surface or enter into the zeolite pores and lead to more aromatics [34]. Nevertheless, the complete deoxygenation of alkylphenols remains incomplete since significant amounts of alkylphenols have been found in the final liquid product. Moreover, the CPO feedstock
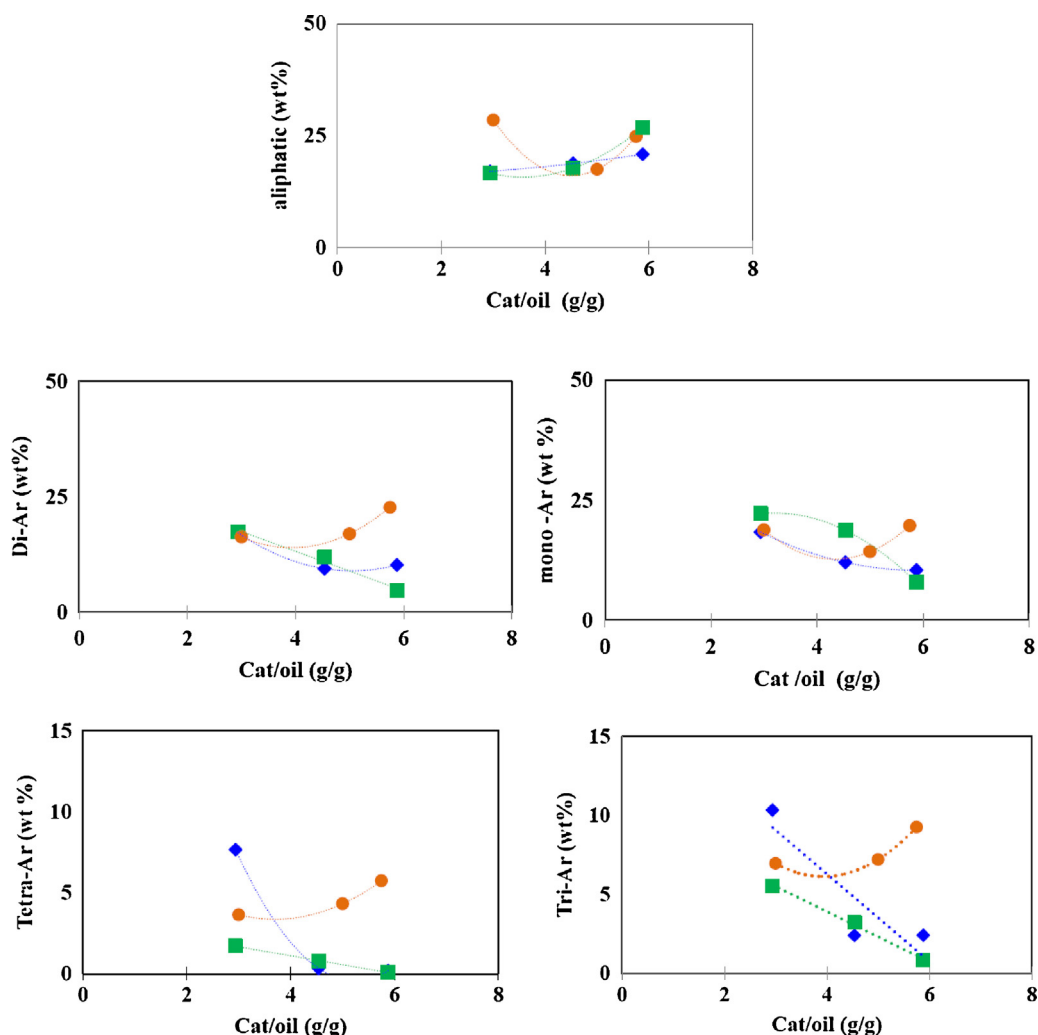
Fig. 3. Aliphatic and aromatic hydrocarbons in gasoline fraction as a function of the Cat/Oil ratio for VGO processing (♦), HDO/VGO co-processing (■) and CPO/VGO co-processing (●).

has an initial higher amount of alkylphenols as compared to HDO, as seen in Table 2. These two effects lead to a higher concentration of alkylphenols in the gasoline fraction by co-processing of CPO compared to HDO (Fig. 4).

Fig. 2 shows that the rate of LCO and bottom fraction conversion is similar for the co-processing of CPO and HDO, but the rate of gasoline production is slightly higher for CPO co-processing than HDO. At the same time the co-processing of HDO yields more LPG and dry gas than CPO. Thus the higher gasoline yield during CPO co-processing compared to HDO can be ascribed to the reduced rate of cracking of the gasoline fraction. This is likely due to the more aromatic character of the CPO gasoline fraction, making it less reactive to further cracking.

Besides these small differences between HDO and CPO co-processing that can be traced back to their composition, the overall performance tends to be similar, with even a slightly higher gasoline yield for CPO over the full range of conversion.

Eliminating a costly hydrogenation step, by adding a catalyst during the pyrolysis makes therefore the co-processing of bio-oils in refineries an even more interesting route for the production of biofuels from lignocellulosic biomass. To further compare the thermal pyrolysis followed by hydrodeoxygenation step and the catalytic pyrolysis route, the overall bio-oil yields are estimated. Table 3 compares a thermal pyrolysis carried out at 450 °C with silica sand with the catalytic pyrolysis at 482 °C with ZSM-5 in the
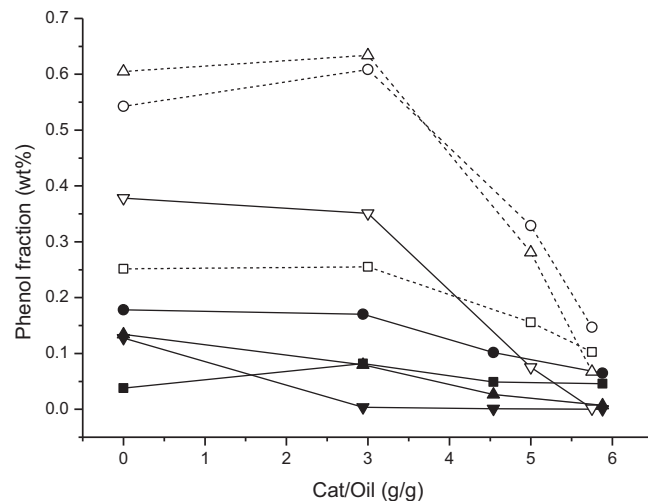

Fig. 4. Alkyl phenols in gasoline fraction as a function of the Cat/Oil ratio HDO/VGO co-processing (filled symbols) and CPO/VGO co-processing (open symbols). (●) C1-phenols, (■) C2-phenols, (▲) C3-phenols, (▼) C4-phenols.

Table 3
Thermal and catalytic pyrolysis in a pilot plant reactor.

	Silica sand	ZSM-5
Temperature	450 °C	482 °C
Biomass/catalyst ratio	16	9
Gases (wt.% biomass)	16	26
Bio-oil (wt.% biomass)	70	58
Solids (wt.% biomass)	11	13
Water (wt.% biomass)	22	29
Organics (wt.% biomass)	48	30
O (wt.% organics)	37	29

same pilot plant reactor. By replacing the silica sand by ZSM-5 the bio-oil yield drops from 70 to 58 wt.% with an even larger drop of the organic fraction from 48 to 30 wt.%. The drop in the bio-oil yield during the catalytic pyrolysis is due to the larger amount of gases formed (+10 wt.%) and solids (+2 wt.%). A further drop in the organic fraction is due to the deoxygenation by the additional formation of water (+7 wt.%). On the other hand, the 48 wt.% of organics from the thermal pyrolysis needs to be further upgraded by a hydrodeoxygenation step. De Mercader et al. [41] obtained approximately 50 wt.% dry yield of HDO by hydrogenation in a batch reactor at 290 bar of H_2 in the temperature range of 230–340 °C. This will thus give an overall yield of the organic fraction of 24 wt.% for the thermal pyrolysis followed by hydrodeoxygenation route compared to 30 wt.% yield derived from the catalytic pyrolysis. As stated above the CPO contains more oxygen than the HDO, but by changing the catalyst during the biomass pyrolysis the oxygen content can be lowered. For example, by using a 10% Co/ZSM-5 Lappas and co-workers reduced the oxygen content by catalytic upgrading of the prolysis vapors in a labscale reactor from 31 wt.% for ZSM-5 to 27 wt.% [34].

5. Conclusions

Thermal pyrolysis oils cannot be (co)-processed directly to liquid fuels, but instead they need first an upgrading step such as hydrodeoxygenation. The obtained HDO oil can then be co-processed with VGO by catalytic cracking. Here instead HDO oil we have used a catalytic bio-oil produced by employing a ZSM-5 catalyst during the biomass pyrolysis step (CPO). CPO can be directly co-processed with VGO without any additional upgrading, if the amount of added bio-oil remains below ca. 20 wt.%. However, little but significant differences in the product distribution and quality have been observed between the co-processing of either HDO or CPO. These differences such as a higher remaining fraction of phenolics in the gasoline or a higher content in aromatics can be reduced by further catalyst development both on the pyrolysis as on the FCC side.

Thus, a hydrogenation step could be eliminated by the addition of a suitable catalyst during the pyrolysis step. The organic yield of the catalytic pyrolysis route is estimated at approximately 30 wt.% as compared to an overall yield for the thermal pyrolysis followed by a hydrodeoxygenation step of 24 wt.%. Bio-oils from catalytic pyrolysis thus offer an interesting potential for the production of bio-fuels via co-processing in a FCC unit both from an energetic as from a technical perspective.

Acknowledgement

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